

THE THEORY OF MOLECULAR DISSOCIATION AND THE FUNDAMENTAL MECHANISMS IN UPPER ATMOSPHERE

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ABSTRACT. In the first article a theoretical formula is developed to estimate the degree of molecular dissociation in upper atmosphere under the action of the ultraviolet light of the sun. In the second article the dissociation of oxygen and nitrogen molecules is discussed and it is found that the oxygen molecules are completely dissociated at a height of about 167 km. *i.e.*, much above E region of the ionosphere, provided we assume a temperature of 300°K and a molecular weight corresponding to the average mass of nitrogen molecules. In the last article the constituents as well as the mechanism of the fundamental processes in ionosphere are discussed.

INTRODUCTION

Many interesting facts have been revealed in recent years from organised spectroscopic studies¹ of night sky and aurora all over the world regarding the constituents present in the upper atmosphere. Whereas hydrogen and helium are found to be absent and ozone confined only in the lower region between 20 to 50 km., it is remarkable that nitrogen and oxygen, along with some percentage of water vapour have been definitely proved to exist in the upper atmosphere, nitrogen being found to be in molecular state from the occurrence of first negative and Vegard Kaplan bands and oxygen in atomic state from the persistent occurrence of the well known green auroral line; all attempts, however, to observe atomic nitrogen and molecular oxygen have been proved unsuccessful. These facts together with the results of the investigation carried out in a previous paper MI² are expected to give a complete picture of the state of affairs in ionosphere. We have found in MI that the theoretical formula for the collision frequency per electron calculated for the interaction between electrons and positive ions agrees satisfactorily well with that obtained from the observation on the reflection coefficient of the radio waves provided we assume that in F layer the number of electrons per cm.³ as revealed by the radio measurement is very nearly equal to the number of ions per cm.³ and in E layer the latter outnumbering the former by a

factor of the order of 100; an immediate conclusion follows, therefore, that the electrons and ions are the chief agents in causing the dispersion and absorption of radio waves in E and F layers, the dispersion being affected directly by the vibration of the electrons whereas the absorption by their encounter with the positive ions.* This high ionic density in E layer of the order of 10^7 is also required for the reconciliation of the estimated electrical conductivity as deduced from wireless observations with the estimates made from the data of terrestrial magnetism.³ [Appleton's original estimation was $n^+ \sim 10^8$ to 10^9 per c.c.]

We have therefore got the following two fundamental problems to solve: Firstly, whether the experimental results of night sky and auroral spectra are to be interpreted as it may seem obvious that oxygen exists in upper atmosphere only in the atomic state, i.e., completely dissociated by sunlight and nitrogen instead of being dissociated get ionised, possibly as a result of fluorescent radiation emitted by the atoms in sun's atmosphere, or oxygen does exist in the molecular state as well, the stronger bands of which being in the ultraviolet regions not being detected so far due to atmospheric absorption and nitrogen may also exist in the atomic state. The problem at present can be answered only by theoretical investigation and will evidently throw much light as to the constituents present in the upper atmosphere. And secondly, how to account for the difference, mentioned, in the number of electrons with respect to positive ions in these ionospheric layers, i.e., in F layer they are equal, whereas in E layer the electrons are in deficiency by a factor 100 over the positive ions. The pursuit of this question together with the knowledge of the laboratory experiments on the collision cross-sections for recombination of electrons and positive ions and for attachment and detachment of electrons to and from the neutral particles shall enable us to understand the fundamental mechanism in ionosphere.

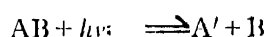
The present paper makes a preliminary theoretical investigation of the above questions. In the first article a general formula is derived for the estimation of the degree of molecular dissociation at different heights in upper atmosphere under the action of the ultraviolet light of the sun. In the second article the formula is applied to find out the degree of dissociation of oxygen and nitrogen molecules, and in conclusion, discussions are given in the light of the above results on the mechanisms of the fundamental processes in ionosphere.

§1. *The equation of molecular dissociation in a non-isothermal system.* Let us consider a system of molecules at an equilibrium temperature T dissociating into their constituent atoms under the action of radiation from a source emitting like a black body at a temperature T_0 which is different from the temperature T of the gas molecules. We shall accordingly obtain a continuous spectrum in absorption starting from a wave length corresponding to the dissociation

* The contribution to the collision frequency as the result of electrons encountering with the neutral particles will be discussed in a subsequent paper.

energy of the molecule and extending to the shorter wave length side, corresponding to the increase of the kinetic energy of the atoms after dissociation. From a study of the absorption and emission coefficients in the continuous spectrum it will be possible to find out an expression for the degree of dissociation of molecules in such a system, which is not in a temperature equilibrium.

The mathematical theory of continuous absorption in case of atoms dissociating into ions and electrons under the action of light has been studied by Milne⁴ by introducing probability coefficients for the mechanism of ionisation by incident radiation and of recombination of electrons with the ions. With the assumption that in the state of thermodynamical equilibrium the number of different types of particles taking part in the reaction must satisfy Saha's equation, Milne obtained a relation between these probability coefficients; the rigorous evaluation of these coefficients separately was, however, carried out by Krammers, Oppenheimer, Gaunt, Sommerfeld and others.⁵ Following Milne, Pannekoek⁶ developed a theory for the dissociation process taking place in a non-isothermal system and obtained a modified Saha's equation, which he applied successfully to explain the observed concentration of free electrons in upper atmosphere at a temperature T caused by the ionisation of molecules into molecular ion and electron under the action of the ultraviolet radiation of the sun, emitting like a black body at a temperature say T_0 , which is different from the temperature T of the ionosphere. We shall also adopt a similar method as that of Milne and Pannekoek in investigating the present problem of dissociation of molecules into their constituent atoms under the influence of external radiation. Let us assume thereby that under the action of light of frequency ν , the molecule AB is dissociated into a normal and an excited atom given respectively by B and A'. Symbolically written it runs as follows:



Let ν_0 be the frequency at which the continuous absorption bands just appear. The energy $h\nu_0$ is thus required for the dissociation of molecule AB into atoms A and B and at the same time for the excitation of the atom A to A', i.e.,

$$h\nu_0 = D + E \quad \dots (1)$$

where D is the heat of dissociation and E that of excitation

Under the action of radiation of frequency $\nu > \nu_0$ the molecule AB is dissociated and a continuous absorption band is formed from ν_0 extending to $\nu = \infty$, the dissociated atoms flying off with the relative kinetic energy

$$\frac{1}{2} MV^2 = h\nu - h\nu_0 \quad \dots (2)$$

where M is the reduced mass given by

$$M = \frac{m_A m_B}{m_A + m_B} \quad (3)$$

and V is the component of the relative velocity in the direction of the lines joining the centres of the atoms.

Let n_{AB} , n_A , and n_B be the equilibrium concentrations of molecules AB , free atoms A and B respectively. The number of absorption processes per second under the action of monochromatic radiation of density ρ_ν from the continuous spectrum is given by

$$n_{AB} \psi_\nu c \rho_\nu dv / h\nu \quad \dots (4)$$

The probability coefficient for absorption ψ_ν has values only for $\nu > \nu_0$.

Whereas the corresponding number of recombination processes is

$$4\pi n_A n_B \beta_\nu \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu\right) \left(\frac{M}{2\pi kT}\right)^{\frac{3}{2}} e^{-MV^2/2kT} V^3 dV \quad \dots (5)$$

where β_ν denotes the probability coefficient for recombination process in the continuous emission band.

By equating the two processes and with the help of (2) we obtain at once the condition of equilibrium as follows:

$$\frac{n_{AB} \psi_\nu c \rho_\nu dv}{h\nu} = 4\pi n_A n_B \beta_\nu \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu\right) \left(\frac{M}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{MV^2}{2kT}} V^2 \frac{h}{m} dv \quad \dots (6)$$

In the case of isotropic radiation of temperature T when ρ_ν is given by the Planck's formula we have the dissociation formula, usually called the reaction isochore, as follows:

$$\frac{n_A n_B}{n_{AB}} = K_0 \quad \dots (7)$$

where K_0 is the equilibrium constant for the dissociation of the molecule AB in atoms A and B and is given by⁷

$$K_0 = G \frac{s}{hr_0} \left(\frac{MkT}{8\pi}\right)^{\frac{1}{2}} e^{-D/kT} \left(1 - e^{-h\omega/kT}\right) \quad \dots (8)$$

$$\text{where } G = \frac{G_A G_B}{G_{AB}} \quad \dots (9)$$

ω = fundamental vibrational frequency of the molecule,

G_A, G_B = statistical weights of the normal quantum state of the free atoms,

G_{AB} = statistical weight of the ground state of the electronic configuration of the molecule, the nuclei being regarded as fixed,

r_0 = equilibrium distance between the atoms,

s = symmetry number of a molecule. It is equal to *unity* if two atoms A and B are intrinsically different whereas it is *two* if the two atoms are identical.

Further we have from Boltzmann's law

$$\frac{n_{A'}}{n_A} = \frac{G_{A'}}{G_A} e^{-E/kT} \quad \dots (10)$$

Thus we obtain

$$\frac{\psi_\nu c \rho_\nu}{h\nu} = \frac{G'_s}{2\pi r_0^2} \frac{MV^2}{kT} e^{-h\nu/kT} \beta_\nu \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu\right) \left(1 - e^{-h\nu/kT}\right) \quad \dots (11)$$

where

$$G' = \frac{G_A G_B}{G_{AB}} \quad \dots (12)$$

Now since

$$\rho_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} ; 1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu = \frac{e^{h\nu/kT}}{e^{h\nu/kT} - 1} \quad \dots (13)$$

we obtain the relation between the coefficients

$$\beta_\nu = \frac{8\pi^2 r_0^2}{c^2 G_s} \frac{kT}{\frac{1}{2} MV^2} \nu^2 \left(1 - e^{-h\nu/kT}\right) \quad \dots (14)$$

When conditions do not correspond to thermal equilibrium the equation (6) must be multiplied by $h\nu$ and integrated over all frequencies, thus ensuring the conservation of energy during the process. We therefore obtain, when the relation (14) is substituted in it,

$$\frac{n_A n_B}{n_{AB}} = K_0 \frac{c^3}{8\pi h} \frac{\int_{\nu_0}^{\infty} \psi_\nu \rho_\nu d\nu}{\int_{\nu_0}^{\infty} \psi_\nu \nu^2 \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu\right) e^{-h\nu/kT} d\nu} \quad \dots (15)$$

For the evaluation of the integrals on the right hand side a knowledge of the absorption coefficient ψ_ν in the continuous region as a function of the

frequency ν is required, which is however very complicated in general for molecules. But in case the absorption coefficient shows a sharp maximum for any particular wave-length falling off rather rapidly on both sides of it, the evaluation of (15) may be easily carried out without much appreciable error by replacing ψ_ν by its maximum value ψ_m and assuming it constant within the short range of integration where only it has positive values. Further, assuming that the velocity distribution of the electrons are given by Maxwell's distribution law at a temperature T , which is different from the temperature T_0 of the black body radiation emitted by the sun and neglecting the effect of the stimulated emission we obtain under the above circumstances,

$$\frac{n_A n_B}{n_{AB}} = K_0 \frac{T_0}{T} e^{-\frac{h\nu_0}{k} \left(\frac{T}{T_0} - 1 \right)} = K_1 \quad \dots (16)$$

$$\text{where } K_1 = \frac{G's}{h\nu_0^2} \left(\frac{M}{8\pi} \right)^{\frac{1}{2}} \frac{k^{\frac{3}{2}} T^{\frac{1}{2}}}{kT} T_0 e^{h\nu_0/kT} e^{-h\nu_0/kT_0} \left(1 - e^{-h\nu/kT} \right) \quad \dots (17)$$

$$\text{or } \frac{n_A' n_B}{n_{AB}} = \frac{G_A'}{G_A} K_0 \frac{T_0}{T} e^{-\left(\frac{h\nu_0}{kT_0} - \frac{1}{kT} \right)} = K_2 \quad \dots (18)$$

$$\text{where } K_2 = \frac{G's}{h\nu_0^2} \left(\frac{M}{8\pi} \right)^{\frac{1}{2}} \frac{k^{\frac{3}{2}} T^{\frac{1}{2}}}{kT} T_0 e^{-h\nu_0/kT_0} \left(1 - e^{-h\nu/kT} \right) \quad \dots (19)$$

If now α is the degree of dissociation, *i.e.*, the fraction of the molecules that are dissociated and P the total pressure of the gas mixture expressed in atmospheres, we can write down the above equation as follows :

$$\frac{\alpha^2}{1-\alpha^2} P = K \quad \dots (20)$$

$$\text{where } K = \frac{1}{10^6} \frac{G's}{h\nu_0^2} \left(\frac{M}{8\pi} \right)^{\frac{1}{2}} \frac{k^{\frac{3}{2}} T^{\frac{1}{2}}}{kT} T_0 e^{-\chi/kT_0} \left(1 - e^{-h\nu/kT} \right) \quad \dots (21)$$

χ = the energy required for dissociation as well as for excitation.

To obtain the degrees of dissociation in the actual ionosphere at a particular height the right hand side of the equation (20) must be multiplied by a factor $e^{-\psi_{\max} N H P}$, where ψ_{\max} is the maximum value of the molecular absorption

coefficient, N' the number of molecules per cm.³ for one atmosphere and H the equivalent height of one atmosphere, and by a factor β the so called dilution factor; the first factor representing the weakening of the active solar radiation due to its absorption caused by the dissociation of the molecules above the layer under consideration and the second one giving the field due to the dilute temperature radiation. β is given by ⁸

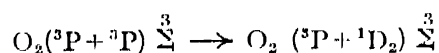
$$\beta = \frac{R^2}{4r^2} \quad \dots \quad (22)$$

where R is the radius of the sun and r the distance from the sun of the point at which the dissociation is calculated.

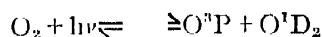
We thus obtain finally the formula for molecular dissociation in upper atmosphere as follows :

$$\frac{x^2}{1-x^2} P = \beta K e^{-\psi_{\max} N' H P} \quad \dots \quad (23)$$

§ 2. (a) *Dissociation of Oxygen Molecules in upper Atmosphere.* Before we apply the formula (23) to the case of oxygen molecules and calculate the degree of dissociation at different heights, let us first summarise the experimental evidences⁹ on the band spectrum of oxygen molecule in the region of continuous absorption in which we are particularly interested in the present paper. The most important bands of O_2 molecule are the Runge-Schuman bands, which starting $\lambda 2000\text{\AA}$ pass to the continuous absorption at $\lambda 1750\text{\AA}$. According to Mulliken it corresponds to the transition



The continuous absorption at $\lambda 1750\text{\AA}$, as pointed out by Herzberg, is due to the photochemical dissociation of O_2 -molecules into a normal 3P and an excited 1D atom according to the process.



the energy required for this being

$$\chi = 7.05V = D + E$$

where $D = 5.09V$ is the heat of dissociation of O_2 -molecules into two normal $O(^3P)$ atoms and $E = 1.96V$, the heat of excitation of $O(^3P)$ atom to the $O(^1D_2)$ state. The

absorption continues up to λ 1250 Å and the portion of it beyond λ 1750 Å corresponds to the increase of the kinetic energy of the constituent atoms after the dissociation process. We shall be chiefly interested in the continuous absorption taking place between λ 1750 Å and λ 1250 Å as a result of the dissociation of the molecules under the action of the ultraviolet radiation from the sun having wave length $\lambda < 3000$ Å. The spectrum in this region has been thoroughly investigated by Ladenburg and Van Voorhis.¹⁰ They find a sharp maxima in the absorption at λ 1450 Å and such that a length of 0.0014 cm. of O₂ at N. T. P. reduced the light of this wave-length to about half of its intensity, *i.e.*, as much as metallic absorption. We have therefore for O₂-molecule assuming $T=300^\circ\text{K}$ (ionosphere) and $T_0=6000^\circ\text{K}$ (sun), $\log \beta K=5.48$, $\log \psi_{\nu}(\text{max})=17.26$; $\log H=5.96$ (corresponding to average mass of nitrogen molecules)¹⁴ and $\log N'=19.39$. It follows therefore

$$\frac{x^2}{1-x^2} = \frac{3 \cdot 10^{-5}}{P} e^{-4.1 \cdot 10^8 P} \quad \dots (24)$$

We tabulate the numerical results in the following :—

P = pressure in Atmosphere, h = height in kilometer, x = degree of dissociation.

10^{-7}	146	10^{-8}
10^{-8}	167	.991
10^{-9}	188	1
10^{-10}	209	1

We find therefore that above 167 km., *i.e.*, much above E layer and at a temperature of 300°K the oxygen molecules are completely dissociated into its constituent atoms. The maximum dissociation occurs at a layer where the total number of molecules per cc. are given by

$$(N/P)_{\text{max}} = \frac{1}{\psi_{\text{max}} H} \sim 6 \cdot 10^{10} \quad \dots (25)$$

(b) *Dissociation of Nitrogen molecules.*⁹ It is found from laboratory experiments that nitrogen is relatively transparent up to λ 1450 Å, where it possesses narrow discrete bands which absorb radiation between 1450–1000 Å. The absorption is complete when the light has traversed a layer equivalent to 40 cm. of the gas at N. T. P. The sharp N₂ bands shows that the molecule is not dissociated by absorption of light λ 1450 Å, which corresponds to the dissociation energy of N₂ but it is simply excited to higher stable states. An examination of the potential curves of nitrogen molecules for normal and excited states also shows that it is quite unlikely that the molecule will be dissociated. A continuous region of spectrum, however,

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appears at about λ 661 Å corresponding to the second ionisation potential 18 which therefore indicates the photo-ionisation of the nitrogen molecule. We therefore assume that the upper atmosphere above the E region will consist n of oxygen in atomic states and nitrogen in molecular state.

§3 *Discussion.* The present paper, as mentioned in the introduction, only a preliminary attempt to estimate the degree of molecular dissociation at different heights in ionosphere, with a view to discuss its constituents and the fundamental mechanism of the process taking place there. We should to point out that our conclusion will be only qualitative, since we have substituted in our numerical calculations the maximum value of the absorption coefficient λ 1450 Å and assumed it constant throughout the range of integration ; a rigorous quantitative investigation should, however, take account of the proper value of the absorption coefficient obtained theoretically ¹¹ as a function of frequency. The results given in the table however, shows that the oxygen molecules remain practically undissociated at a height of 146 km. and then the dissociation suddenly almost completed at a height of 167 km. This is due to the simplified assumptions we have just mentioned. Considering the variation of the absorption coefficient with wave-length we can easily find that the dissociation will spread over a height of the order of 30 km., i.e., dissociation at each level will take place earlier by this amount of height and it will therefore be quite probable that the oxygen molecules are dissociated at least quite appreciably even up to a height of 130 km. Further the number of oxygen atoms as given by (10) agrees fairly well with the tentative estimation of Chapman and is sufficient for the production of the requisite number of metastable atoms which are required to explain the intensity of the green light (λ 5577 Å) of the night sky spectrum as observed particularly by McLennan and Rayleigh. The layer of atomic oxygen lying at a height above the E region is thus a possible source of the greenlight. These results, that is, the upper atmosphere above a height of E layer consists mainly of atomic oxygen and molecular nitrogen (also some percentage of water vapour), when incorporated in the investigations of an earlier MI, as mentioned in the introduction enable us to analyse the fundamental mechanisms as regards the various processes taking place in ionosphere. For the purpose we collect first the relevant data regarding these layers :

Layer	height in km.	n in cc.	n^+ in cc.	N in cc.	V in cm/per sec.	Δ per sec.	T in degree Abs.
F layer	~300	10^8	10^6	10^6	$1.7 \cdot 10^7$	10^3	10^3
E layer	~100	10^7	10^7	10^{14}	$9.5 \cdot 10^6$	$2 \cdot 10^5$	$3 \cdot 10^2$

Fundamental process.	cross section in cm ² .	velocity variation.	pressure variation.
$N_2^+ + e \rightarrow N_2$ (recombination) ...	$5 \cdot 10^{-17}$	$1/v^2$	none
$O + e \rightarrow O^+ + h\nu$ (attachment) ...	$1.3 \cdot 10^{-16}$	$1/v^2$	none
$O + O \rightarrow O_2 + e$ (detachment)

The data for n and n' are taken from the paper MI, and N , the total number of particles per cm³ calculated after Maris and Hulbert¹², assuming that the mean molecular mass of the atmosphere is equal to that of molecular nitrogen. The cross-sections for the fundamental processes, calculated for a temperature of 300° K, are reproduced from a paper by Bradbury.¹³

Now what are the reasons that in E layer the number of ions per cm³ outnumber the electronic concentration by a factor of the order of 100 and in F layer they are equal and that the collision frequency per electron as measured from the reflection coefficient of radio waves correspond to the collision of the electrons with the positive ions only? The answer to this question will give us an understanding of the processes in these layers. It can, however, be better understood with reference to the consideration of the magnitude of probabilities of these different processes. Since the rate of loss of electron density due to recombination and attachment processes at night are given respectively by¹³

$$\frac{dn}{dt} = -v Q^r(v) n^2 \quad \text{and} \quad \frac{dn}{dt} = -v Q^a(v) N n$$

where v is velocity of the electron and $Q(v)$ the effective cross-section for electrons of velocity v , we obtain the ratio of the loss of the particles due to these processes as given by

$$\frac{\text{Loss due to recombination}}{\text{Loss due to attachment}} = \frac{n}{N} \frac{Q^r(v)}{Q^a(v)}$$

$$\sim 10^{-4} \quad \text{for E layer}$$

$$\sim 4 \cdot 10^2 \quad \text{for F layer}$$

The rate of recombination per electron in E and F layers are $4.7 \cdot 10^{-3}$ and $2.3 \cdot 10^{-4}$ respectively, the coefficients of recombination $\alpha = Q^r(v)/v$ being

$4.7 \cdot 10^{-10}$ and $2.5 \cdot 10^{-10}$.* This slow rate of recombination, which is also required from the observations, together with the fact that the observed collision frequency per electron is due mainly to its encounter with the positive ions only, the neutral particles being practically out of the scene, strongly suggests that the disappearance of electrons in both E and F layers during the night is caused chiefly by the recombination of electrons with positive ions. An examination of the rate of loss of electrons by recombinations and that by attachment offers then an easy explanation for the ratio of the number of electrons to that of the ions in E and F layers as mentioned above. The preponderance of attachment process over the recombination and the deficiency of electrons over the ions by a factor 100 in E layer show that the number of electrons initially produced by the ionisation of molecules shall set up a sort of local equilibrium with the negative ions as a result of rapid attachment and detachment processes[†] to and from the neutral particles until their ratio has reached the stationary value 300,† while the loss of electrons, however, being ultimately governed by their recombination with the ions. In F layer on the other hand the recombination is more rapid than the attachment and therefore the numbers of electrons initially produced shall also be equal to the numbers of positive ions, there being practically no attachment to the neutral particles.

The quantitative investigation of the problem of dissociation as well as of the fundamental processes in ionosphere is reserved for subsequent communication.

I am grateful to Professor M. N. Saha for kindly drawing my attention to this interesting problem of ionosphere and to Professor D. M. Bose for his interest and encouragement.

* The effective coefficients of recombination for E and F layers as defined by³

$$\alpha' = \alpha \left(1 + \frac{n^-}{n^+} \right),$$

n^- being the negative ion density, are $1.4 \cdot 10^{-7}$ and $2.5 \cdot 10^{-10}$ respectively.

† Massey has also recently drawn attention to this problem from the consideration of the magnitudes of various collision processes in ionosphere. The present paper, though it was nearly ready for publication, has undergone a little alteration after Massey's paper. It follows from his result that the attachment should also be equally important in F layer and there would be nearly the same equilibrium ratio between the electrons and ions as in E layer as a result of attachment and detachment processes. But as the concentration of electrons in F layer is equal to that of ions, Massey passes over the difficulty by concluding that the gas or gases present there have very little electron affinity and they are therefore nitrogen. This conclusion, however, cannot be reconciled with the observed facts that in ordinary aurora the green line of atomic oxygen (λ 5577Å) and in sunlit aurora the red oxygen line λ 6300. Å is prominently strong, showing therefore the great abundance of oxygen atoms even up to a height of 1000 km. For a quantitative elucidation of this important point we should investigate the whole problem from a consideration of the statistical equilibrium between all the elementary fundamental processes in ionosphere.

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